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Polybrominated Diphenyl Ethers and Other Persistent Organic Pollutants in Serum Pools from the National Health and Nutrition Examination Survey: 2001–2002

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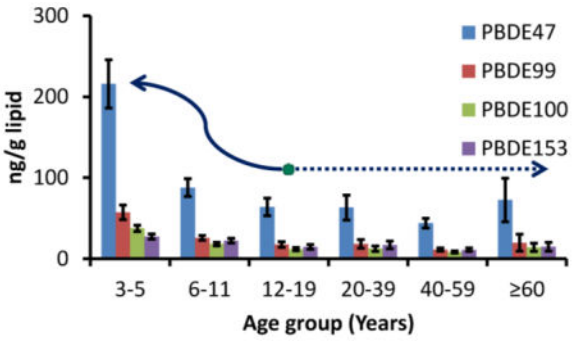
Abstract

Polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and persistent pesticides have been measured in serum pools from participants 3–5, 6–11, 12–19, 20–39, 40–59, and ≥60 years of age from the 2001–2002 National Health and Nutrition Examination Survey. For 2,2′,4,4′-tetrabromodiphenyl ether (PBDE-47), the unweighted (not adjusted for sampling weights) arithmetic mean concentration (±95% confidence interval) was 3.4 times higher in 3–5-year-olds (216 ± 30 ng/g of lipid) than in 12–19-year-olds (64 ± 11 ng/g of lipid), with no apparent change with increasing age for adults ≥20 years of age. By contrast, unweighted arithmetic mean concentrations of traditional persistent organic pollutants (POPs) such as hexachlorobenzene (HCB) and 2,2′,3,3′,4,4′,5,5′-octachlorobiphenyl (PCB194) were 2- and 20-fold higher, respectively, in persons ≥60 years than in 12–19-year-old adolescents. Findings suggest higher exposures to PBDEs but lower exposures to traditional POPs in 3–5-year-old children than in adults.

Graphical Abstract



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The authors declare no competing financial interest.

Supporting Information

Table giving the unweighted arithmetic mean concentrations (nanograms per gram of lipid) with 95% confidence intervals of select persistent organic pollutants in pooled serum samples by age category from the 2001–2002 NHANES. This material is available free of charge via the Internet at http://pubs.acs.org.

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) make up a class of persistent and bioaccumulative brominated flame retardants. Technical pentaBDE has been used in applications such as furniture and the polyurethane pad used under wall-to-wall carpets, while the octaBDE and decaBDE products have been used in hard plastics such as the housing of electrical appliances. Other than a few hexaBDEs, the congeners present in technical octaBDE and decaBDE are normally not detected in human samples because of their short biological half-lives.[1] On the other hand, congeners present in technical pentaBDE (tri- to hexaBDEs) are commonly detected in people.[2,3]

PBDEs and other persistent organic pollutants (POPs) [e.g., polychlorinated biphenyls (PCBs) and organochlorine pesticides] have mainly been measured in adult populations or in cord sera collected at birth because blood is more difficult to collect from children than adults. Interestingly, in American homes, indoor dust concentrations of certain PBDE congeners are orders of magnitude higher than those of certain PCBs[4–6] likely because PCBs and organochlorine pesticides were phased out from industrial production and use in the 1970s and are uncommon in American homes today. Assessing human exposure to PBDEs and other POPs among the general population may provide useful information for understanding the pathways of exposure to these compounds, including vulnerable population groups such as children and the elderly.

The National Health and Nutrition Examination Survey (NHANES) is an ongoing survey designed to evaluate the health and nutrition status of the civilian noninstitutionalized U.S. population and includes the exposure assessment to select environmental chemicals, including POPs.[2,3] However, the NHANES lacks data on POPs exposure for children younger than 12 years of age. To fill this gap, we used serum pools prepared from individual samples collected from 3–11-year-old children, adolescents, and adults participating in the 2001–2002 NHANES, already used for assessing exposure to other organic chemicals, including polyfluoroalkyl compounds[7,8] and phenols such as bisphenol A,[9] to characterize exposure to PBDEs, PCBs, and persistent pesticides in toddlers (3–5 years of age), children (6–11 years of age), adolescents (12–19 years of age), adults (20–39 and 40–59 years of age), and seniors (≥60 years of age).

MATERIALS AND METHODS

Pooling Strategy

NHANES is a multistage, probability sampling of the civilian, noninstitutionalized U.S. population. Oversampling of certain population subgroups is performed to increase the reliability and precision of estimates for those groups. Sample weighting adjusts for unequal selection probability and is used to produce correct population estimates of means, percentiles, and other descriptive statistics. However, we used equal amounts of each individual sample to create pools, and this approach did not allow us to consider sampling weights. As a result, our estimates cannot be considered representative of the general U.S. population, but because the individual samples used to prepare the pools originated from the

2001–2002 NHANES, which was designed to be representative of the noninstitutionalized U.S. population, the pools provide good coverage of the U.S. population.

Of the 3199 available individual 2001–2002 NHANES serum samples, we used 2768 stratified into 36 demographic groups {two sex, six age (3–5, 6–11, 12–19, 20–39, 40–59, and ≥60 years of age), and three race/ethnicity [Mexican American (MA), non-Hispanic black (NHB), and non-Hispanic white (NHW) (subjects belonging to other race/ethnicity groups were excluded)] categories} to create 78 pools (Table S1 of the Supporting Information). Thirty-four individual serum samples were included in each pool for subjects ≥12–19 years of age except where noted (Table S1 of the Supporting Information). For the younger age groups, pools were formed from 21 (3–5 years of age) and 57 (6–11 years of age) individual samples. Although using different numbers of samples per pool is not optimal, the variable number of samples per pool was driven by the availability of serum. The National Centers for Health Statistics Institutional Review Board reviewed and approved the study protocol. All participants gave informed written consent; parents or guardians provided consent for participants <18 years of age.

The individual serum samples were thawed and mixed before the desired serum amounts were weighed into 2 oz precleaned KaptClean Qorpak borosilicate glass bottles with Teflon PTFE-lined polypropylene screw caps. Serum was transferred using a new glass pipet for each sample. The total weight of each pool was determined as the difference in weight between the empty bottle and the bottle plus the serum. Each aliquot was labeled with the study and serum pool identification number and target analytes.

The analytical methodology has been published previously.[10] Two grams of serum was used for the measurements of PBDEs, PCBs, and persistent pesticides, and the pools were randomly assigned to 24 sample batches for analysis; each analytical batch contained three quality control and three blank samples comprised of bovine serum (Gibco Inc., Grand Island, NY) diluted 1:40 with water; this dilution was made to reduce any target analytes in the blank serum to a level 1 order of magnitude lower than the limit of detection (LOD). All analytical data were corrected by subtracting the median blank value. The LODs were determined as the higher of (1) 3 times the standard deviation of the amount present in blanks or (2) the instrumental LOD defined as the injected amount known to produce a gas chromatography/isotope dilution–high-resolution mass spectrometry signal-to-noise ratio of >10.

Statistical Methods

Statistical analysis was performed using SAS 9.3 or SAS Enterprise Guide 5.1 (SAS Institute Inc., Cary, NC). Concentrations below the LOD were substituted with the LOD/√2. Unweighted arithmetic mean concentrations (nanograms per gram of lipid) by analyte were calculated using the SAS procedure “Proc Univariate”, collapsing the sex and race/ethnicity variables to increase the number of measurements per remaining age group. The formulas for calculating the lower and upper 95% confidence limits (95% CI) of the unweighted arithmetic means were

$$\text{lower } 95\%\ \text{CI} = \text{mean} - \text{standard error} \times t(1-\alpha/2,\ \text{DF})$$
$$\text{upper } 95\%\ \text{CI} = \text{mean} + \text{standard error} \times t(1-\alpha/2,\ \text{DF})$$

where mean is the unweighted arithmetic mean, $t(1 - \alpha/2, \text{DF})$ is a Student's t-test-distributed critical value, α is equal to 0.025, and DF is equal to the number of pools minus one. To increase the statistical power for studying potential concentration changes with age group, sex and race/ethnicity variables were collapsed to increase the number of samples per age group.

Of note, these unweighted arithmetic means are not comparable to weighted geometric means as reported in the Centers for Disease Control and Prevention's National Reports on Human Exposure to Environmental Chemicals.[2] Also, the statistical analyses performed herein are subject to several limitations, including (1) the use of univariate methods involving multiple comparisons that can lead to spurious statistically significant results, (2) small sample sizes for all demographic groups that can lead to low statistical power and hence the failure to identify statistically significant differences, (3) the use of unweighted arithmetic means to compare demographic groups whereas the 2001/02 NHANES individual samples forming pools are not necessarily normally distributed and tend to be skewed to higher values, (4) a variable number of samples per pool across age groups, which affects the variability of pool measurements that in turn can affect the reliability of comparisons between age groups, and (5) the inability to calculate design effects because pools were formed across the design cells of the 2001–2002 NHANES.

RESULTS

A total of 48 POPs, including PBDEs, PCBs, and persistent pesticides, were measured in 2001–2002 NHANES pooled sera. For further statistical evaluation, only analytes with detection frequencies of ≥50% in all demographic groups were considered (Table 1). For the age-related analysis, the sex and race/ethnicity groups were collapsed, providing the maximal number of pools available per age stratum to be able to conduct meaningful statistical comparisons among age categories: 3–5 (N = 12), 6–11 (N = 12), 12–19 (N = 19), 20–39 (N = 13), 40–59 (N = 10) and ≥60 years of age (N = 12).

Pools made from persons between 6–11 and 12–19 years of age had the lowest unweighted arithmetic mean concentrations of traditional POPs such as PCBs, 2,2-bis(2-chlorophenyl)-1,1-dichloroethene (p,p'-DDE), hexachlorobenzene (HCB), and 2,2′,4,4′,5,5′-hexabromobiphenyl (PBB153, lowest in 3–5-year-olds); the 95% CI of the unweighted arithmetic means overlapped, suggesting no concentration differences between these age groups for traditional POPs (Figures 1–3 and Table S2 of the Supporting Information). PCBs, p,p'-DDE, HCB, and PBB-153 serum concentrations increased consistently with increasing age [from 12–19 to ≥60 years of age (Figures 1–3 and Table S2 of the Supporting Information)]. Persons ≥60 years of age had unweighted arithmetic mean concentrations 2-fold (HCB) to 20-fold higher (PCB194) than those of 12–19 year-old-adolescents (Figures 1 and 2 and Table S2 of the Supporting Information). The 95% CI of the unweighted arithmetic mean concentration was higher for the 3–5-year-olds than for the 6–11-year-olds

for PCB74 (74% higher), and the 95% CIs for other traditional POPs overlapped for these age groups. In contrast, 3–5-year-old children had the highest unweighted arithmetic mean concentrations of PBDEs (Figure 3 and Table S2 of the Supporting Information). The decreases in unweighted arithmetic mean concentration between the 3–5- and 12–19-year-old groups were 1.9-fold (PBDE-153) to 3.4-fold (PBDE-47). No consistent associations with age were observed for PBDEs between adolescents (12–19 years of age) and the oldest age group (≥60 years of age).

DISCUSSION

We detected 17 POPs in more than 50% of the pools analyzed from any demographic group examined, suggesting prevalent exposure to these compounds (Table 1). We collapsed the race/ethnicity and sex groups to form a total of six age groups with 10–19 serum pools per age group covering the age range from toddlers to seniors. This collapse of race/ethnicity could affect some of the estimates, especially for *p,p′*-DDE and, to a lesser extent, some PCBs, known to be found at higher (*p,p′*-DDE) or lower (PCBs) concentrations in Mexican Americans than in other race/ethnicity groups.[11] Between sex categories we expect only marginal differences.

The concentrations of traditional POPs were generally lowest in children 6–11 and 12–19 years of age compared to those of adults. However, toddlers (3–5 years of age) had significantly higher PCB74 concentrations than older children and adolescents, maybe as a result of exposure through breast milk. However, because only pools were analyzed, discerning if children who nursed in infancy had higher concentrations of POPs than other children is impossible. The concentration of all POPs excluding PBDEs increased continuously from 12–19 to ≥60 years of age as had been documented previously.[11] For example, the concentrations of PCB153 and *p,p′*-DDE were 900 and 350%, respectively, higher in the ≥60-year-old adults than in the 12–19-year-old adolescents (Figures 1 and 2 and Table S2 of the Supporting Information). This is a reflection of older subjects being exposed continuously during their life to these persistent contaminants and at higher daily intake rates in the past when environmental levels of these POPs were higher than they are today.[12,13] Younger individuals have experienced lower exposures in their shorter life spans, resulting in their body burden being lower than that of older individuals.

In the case of PBDEs, we observed similar concentrations with increasing age from 12–19 to ≥60 years of age, which is a result of similar exposure to the entire population because PBDEs have been in commercial use until recently and were still being used in 2001–2002 when the samples used for this study were collected. However, it is likely that such a pattern will develop with time from the discontinuation of commercial production, if the half-lives of PBDEs are sufficiently long. At present, the only experimentally measured biological half-lives of PBDEs are those for PBDE-183 (3 months) and PBDE-209 (2 weeks).[1]

Children in the youngest age group (3–5 years of age) had higher concentrations of PBDEs than other age groups (Figure 3 and Table S2 of the Supporting Information). For example, concentrations of PBDE-47 in the 3–5-year-olds were 150 and 240% than those in the 6–11- and 12–19-year-olds, respectively. Higher concentrations of PBDEs in children of this age

have also been reported for an Australian population.[14] This observation is likely explained by exposure to residential dust through hand-to-mouth behavior at a young age,[14,15] although the possibility of exposure through nursing cannot be excluded. Indoor dust collected in the United States contained 430 ng of PBDE-47/g of dust [range of 230–3000 (N = 10)], which was >30-fold higher than that, for example, in Germany, which had the lowest concentration [<14 ng/g of dust, range of <14–22 (N = 10)] among four countries investigated,[5] suggesting that dust ingestion in North America may be a relatively more important PBDE exposure pathway than in other countries. The U.S. EPA[16] estimates that a child (2.5–6 years of age) ingests 50–100 mg of dust per day while adult exposures are much lower (0.6 mg of dust/day); however, it must be emphasized that such estimates are associated with large uncertainties. Therefore, the decrease in concentration seen after the 3–5-year-old group could be explained by a reduction in the ingestion rate of indoor dust and dilution of the PBDEs in an increasing body size as the child is growing up and/or elimination of PBDEs through metabolism.

In summary, our findings suggest higher exposures to PBDEs but lower exposures to traditional POPs in 3–5-year-old children compared to adults in the United States. Remediation by replacing upholstered furniture and/or foam pads under wall-to-wall carpets may or may not be an effective strategy for reducing PBDE exposure because recycled foam potentially used in such products may contain PBDEs.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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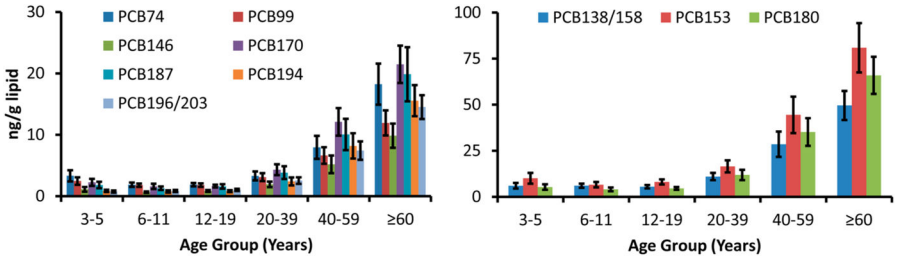

Figure 1.

Unweighted arithmetic mean concentrations (nanograms per gram of lipid) with 95% confidence intervals of serum pools for polychlorinated biphenyls (PCBs). Race/ethnicity and sex categories collapsed into six age categories. IUPAC names and compound abbreviations are given in Table 1.

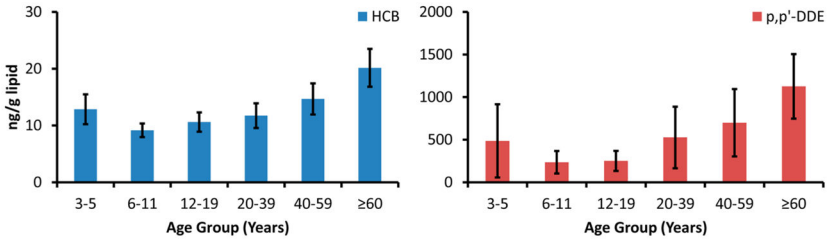

Figure 2.

Unweighted arithmetic mean concentrations (nanograms per gram of lipid) with 95% confidence intervals of serum pools for hexachlorobenzene (HCB) and *p,p′*-dichlorodiphenyldichloroethylene (*p,p′*-DDE). Race/ethnicity and sex categories collapsed into six age categories.

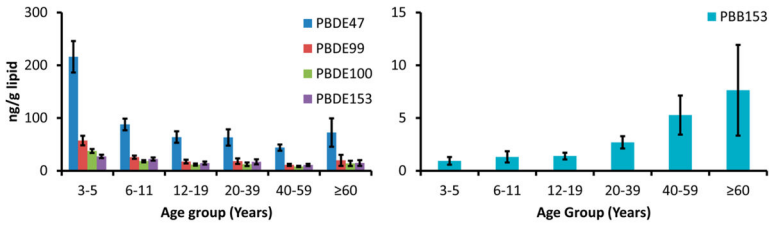

Figure 3.

Unweighted arithmetic mean concentrations (nanograms per gram of lipid) with 95% confidence intervals of serum pools for polybrominated diphenyl ethers (PBDEs) and polybrominated biphenyls (PBB). Race/ethnicity and sex categories collapsed into six age categories. IUPAC names and compound abbreviations are given in Table 1.

Table 1

International Union of Pure and Applied Chemistry (IUPAC) Names and Common Abbreviations for Persistent Organic Pollutants Detectable in >50% of Any Demographic Group (gender, age, and race/ethnicity) of 2001/02 NHANES Pooled Serum Samples

IUPAC name and common abbreviation	detection frequency (%) [mean (range)]
Brominated Flame Retardants (BFRs)	
2,2′,4,4′-tetrabromodiphenyl ether (PBDE47)	100 (100–100)
2,2′,4,4′,5-pentabromodiphenyl ether (PBDE99)	100 (100–100)
2,2′,4,4′,6-pentabromodiphenyl ether (PBDE100)	100 (100–100)
2,2′,4,4′,5,5′-hexabromodiphenyl ether (PBDE153)	100 (100–100)
2,2′,4,4′,5,5′-hexabromobiphenyl (PBB153)	95 (50–100)
Polychlorinated Biphenyls (PCBs)	
2,4,4′,5-tetrachlorobiphenyl (PCB74)	100 (100–100)
2,2′,4,4′,5-pentachlorobiphenyl (PCB99)	100 (100–100)
2,2′,3,4,4′,5′- and 2,3,3′,4,4′,6-hexachlorobiphenyl (PCB138–158)	100 (100–100)
2,2′,3,4′,5,5′-hexachlorobiphenyl (PCB146)	96 (50–100)
2,2′,4,4′,5,5′-hexachlorobiphenyl (PCB153)	100 (100–100)
2,2′,3,3′,4,4′,5-heptachlorobiphenyl (PCB170)	100 (100–100)
2,2′,3,4,4′,5,5′-heptachlorobiphenyl (PCB180)	100 (100–100)
2,2′,3,4′,5,5′,6-heptachlorobiphenyl (PCB187)	100 (100–100)
2,2′,3,3′,4,4′,5,5′-octachlorobiphenyl (PCB194)	94 (50–100)
2,2′,3,3′,4,4′,5,6′- and 2,2′,3,4,4′,5,5′,6-octachlorobiphenyl (PCB196–203)	95 (50–100)
Persistent Pesticides	
hexachlorobenzene (HCB)	100 (100–100)
p,*p*′-dichlorodiphenyldichloroethylene (*p*,*p*′-DDE)	100 (100–100)